

UNCLASSIFIED

AD NUMBER
AD106967
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM No foreign distribution
AUTHORITY
ONR ltr., 6 Oct 1977

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED
AD06967

Armed Services Technical Information Agency

Reproduced by

DOCUMENT SERVICE CENTER

KNOTT BUILDING, DAYTON, 2, OHIO

This document is the property of the United States Government. It is furnished for the duration of the contract and shall be returned when no longer required, or upon recall by ASTIA to the following address: Armed Services Technical Information Agency, Document Service Center, Knott Building, Dayton 2, Ohio.

NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY IMPLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

UNCLASSIFIED

AD NO. 106967

ASTIA FILE COPY

UNCLASSIFIED

NON-SOLVATED ALUMINUM HYDRIDE

Technical Report to the Office of Naval Research
Contract ONR-494(04)

By

M. John Rice, Jr.

With the Assistance of

George Chizinsky

FC

Department of Chemistry
TUFTS UNIVERSITY
Medford 55, Mass.

1 August 1956

UNCLASSIFIED

ONR-491(04)
Technical Report
1 August 1956

DISTRIBUTION LIST

<u>Addressee</u>	<u>No. of Copies</u>
Commanding Officer Office of Naval Research Branch Office The John Crerar Library Building 86 East Randolph Street Chicago 1, Illinois	1
Commanding Officer Office of Naval Research Branch Office 346 Broadway New York 13, New York	1
Commanding Officer Office of Naval Research Branch Office 1030 E. Green Street Pasadena 1, California	1
Commanding Officer Office of Naval Research Branch Office Navy #100 Fleet Post Office New York, New York	2
Director Naval Research Laboratory Washington 25, D. C. Attn: Technical Information Officer	6
Chief of Naval Research Washington 25, D. C. Attn: Code 425	2
Technical Library OASD (R&D) Pentagon Room 3E1065 Washington 25, D. C.	1
Technical Director Research and Development Division Office of the Quartermaster General Department of the Army Washington 25, D. C.	1

-ii-
DISTRIBUTION LIST
Cont.

Research Director Chemical & Plastics Division Quartermaster Research & Development Command Natick, Massachusetts	1
Scientific Director Quartermaster Research & Development Command Natick, Massachusetts	1
Director Office of Scientific Research Air Research & Development Command P.O. Box 1395 Baltimore 3, Maryland	1
Office of the Chief of Ordnance Department of the Army Washington 25, D. C. Attn: ORDTB-P3	1
Office of Chief of Staff (R&D) Department of the Army Pentagon 38516 Washington 25, D. C. Attn: Chemical Advisor	1
Director, Naval Research Laboratory Washington 25, D. C. Attn: Chemistry Division	2
Chief, Bureau of Ships Department of the Navy Washington 25, D. C. Attn: Code 331	2
Chief, Bureau of Aeronautics Department of the Navy Washington 25, D. C. Attn: Code TD-4	2
Chief, Bureau of Ordnance Department of the Navy Washington 25, D. C. Attn: Code Ad-3	2

-iii-
DISTRIBUTION LIST
Con't.

ASTIA Document Service Center Knott Building Dayton 2, Ohio	5
Director of Research Signal Corps Eng. Laboratories Fort Monmouth, New Jersey	1
U. S. Naval Radiological Defense Lab. San Francisco 24, California Attn: Technical Library	1
Naval Ordnance Test Station China Lake, California Attn: Head, Chemistry Division	1
Office of Ordnance Research 2127 Myrtle Drive Durham, North Carolina	1
Technical Command Chemical Corps Chemical Center, Maryland	1
Brookhaven National Laboratory Chemistry Division Upton, New York	1
Atomic Energy Commission Research Division Chemistry Branch Washington 25, D. C.	1
Atomic Energy Commission Library Branch Technical Information ORE Post Office Box E Oak Ridge, Tennessee	1
Office of Technical Services Department of Commerce Washington 25, D. C.	1
Commanding Officer Office of Naval Research Branch Office 495 Summer Street Boston 10, Mass.	2

-iv-
DISTRIBUTION LIST
Con't.

Dr. A. E. Finholt Department of Chemistry St. Olaf College Northfield, Minnesota	1
Dr. H. I. Schlosinger Department of Chemistry University of Chicago Chicago, Illinois	1
Dr. J. C. Warf Department of Chemistry University of Southern California Los Angeles 7, California	1
Drs. W. H. Nebergall and J. S. Peake Department of Chemistry Indiana University Bloomington, Indiana	1
Dr. A. Burg Department of Chemistry University of Southern California Los Angeles 7, California	1
Olin-Mathieson Chemical Corp. (Research Lab) P. O. Box 480 Niagara Falls, New York Attn: Dr. C. C. Clark	1
Dr. C. B. Jackson & Mr. R. A. Mulholland Callery Chemical Company Callery, Penn.	2
Dr. Edwin F. Orleman, Radiation Laboratory University of California P. O. Box 808 Livermore, California	1
Dr. George Schaeffer University of St. Louis St. Louis, Missouri	1
Dr. C. A. Brown Department of Chemistry Western Reserve University Cleveland, Ohio	1

v.

ABSTRACT

The preparation of non-solvated aluminum hydride is described. The properties of the compound are described and results of X-ray diffraction studies are given.

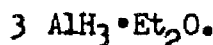
1.

A. Introduction

The classical method for preparing aluminum hydride is based on the reaction between ether solutions of aluminum chloride and lithium aluminum hydride (1).



This results in an ether solution of aluminum hydride which, within a short time, comes out of solution as a curdy, white solid which is presumed to be polymeric. The solid gives up some of the co-ordinated ether when treated under vacuum, yielding a material of the composition:



Further vacuum treatment and heating decompose the material rather than removing the remaining ether; pure, non-solvated aluminum hydride must be prepared by some other method. Stecher and Wiberg (2) prepared non-solvated aluminum hydride by treating aluminum alkyls in a hydrogen glow discharge. The product was not pure in that all possible aluminum alkyl hydrides were present and separation was carried out by preparing coordination compounds with amines. Also, the method was not practical for preparing useful quantities of pure aluminum hydride.

Several possible structures of aluminum hydride have been proposed. Each of these neglects the co-ordinated ether, however, which is present in the polymeric form. Wiberg (2) first proposed a linear structure in which the aluminum atoms are connected by single hydrogen bridges:



A later proposal by Wiberg (3) was essentially a simplified version of one proposed earlier by Lonquet-Higgins (4) in which hexagons of aluminum atoms lie in a plane, with two bridge hydrogens between aluminum atoms lying above and below the plane of the hexagons.

The present investigation was carried out as a portion of a more general study of aluminum hydride. The specific purpose of this study was to prepare non-solvated aluminum hydride and to attempt to determine its structure.

B. Experimental and Results

Two basic ideas were used in attempting to prepare non-etherated aluminum hydride; first, various solvents other than diethyl ether were used in preparing the aluminum hydride and second, aluminum hydride solutions in diethyl ether were run in to various solvents and the solvent mixtures removed by vacuum.

Both diisopropyl ether and dimethyl sulfide were tried as solvents in lieu of diethyl ether. In each case reaction was incomplete and in the case of dimethyl sulfide a mixture of products was obtained indicating that undesirable side reactions were occurring. These results gave no indication of success and this type of attack was abandoned.

A great deal of time and effort were devoted to studying the possibility of ridding aluminum hydride of ether by treatment with other inert solvents. At first, the study consisted of adding ether solutions of aluminum hydride to various solvents and removing the mixed solvents in vacuo in order to single out the most promising "ether remover". Table 1 lists the results obtained with various solvents under similar conditions

Table 1

<u>Precipitating Solvent</u>	<u>Volume Solvent Per Gram $AlCl_3$</u>	<u>Remarks</u>	<u>%H</u>	<u>% Al</u>
Benzene	19 ml.	Evacuated for a few hours at room temp.	1.76	14.70
Dioxane	19 ml.	"	1.89	20.42
Pentane	19 ml.	"	5.15	48.67
Tetrahydrofuran (no ppt.)	20 ml.	"	1.57	15.7
Carbon disulfide	20 ml.	"	Exploded	
		Theoretical	10.0	90.0

The results of these early experiments showed that pentane was the most promising of all the solvents tried. Accordingly, varying conditions were tried until it was found possible to obtain non-etherated aluminum hydride. It was found that the volume of inert solvent used was critical. At least, 100 ml. of pentane per gram of $AlCl_3$ (used in making the AlH_3) was necessary.

A typical preparation is as follows:

The apparatus used in the preparation of the non-solvated hydride is shown in Figure 1. The reaction flask B was taken into a drybox and the desired amount of aluminum chloride weighed out carefully on a triple beam balance. The flask was tightly stoppered and then connected to the apparatus. A quantity of ether,

sufficient to provide approximately 10 ml. of ether per gram of AlCl_3 , was added slowly through the top of the condenser A. A drying tube was added to the top of the condenser and the solution stirred until all of the AlCl_3 had dissolved. A stoichiometric amount of LiAlH_4 solution was added and after briefly stirring the LiCl was allowed to settle. Nitrogen pressure was applied at the top of the condenser to force the AlH_3 solution through the fritted glass filter C into flask D containing pentane. The solution was run down a wire in a thin film into the pentane which was stirred by a magnetic stirrer. The AlH_3 precipitated immediately on contact with the pentane. After addition of the AlH_3 solution the reaction flask and filter were removed from the system. The solvent mixture was removed by vacuum and collected in the cold trap E. It was usually necessary to maintain the AlH_3 under vacuum for at least 12 hours at room temperature in order to remove all the ether. Ether removal was facilitated by heating the flask to 50°C . and by repeatedly grinding the product with the magnetic stirrer. When the pressure in the system became less than 2 μ , the system was filled with nitrogen, flask D removed and stoppered and the flask removed to a nitrogen drybox where it could be handled safely. Freshly prepared samples were white, fluffy, pyrophoric powders with a low bulk density. The samples were fairly stable at room temperature. Stability seemed to be related to purity; the container with the most pure sample developed negligible hydrogen pressure over a period of weeks while some samples containing chloride turned jet black in a few days.

Analysis of the products was carried out using standard procedures. Hydrogen was determined by evolution with water and aluminum by the 8-hydroxyquinoline method. A test for chloride was made using silver nitrate; if more than a trace of chloride was present, it was determined by the Volhard method using eosin as an indicator. All samples gave a positive flame test for lithium but lithium was present in too small amounts to be determined by wet methods.

Densities of aluminum hydride samples were determined in a helium densitometer similar to one described by Schumb (5). The density as a function of ether content is shown in Figure 2. The density of the pure hydride was determined to be 1.718 g/ml, but this value was subject to some error due to the small weight of sample used in the measurement.

X-ray powder patterns were made of many samples using Cu-K α radiation in a General Electric XRD-4 apparatus. No patterns were obtained unless the samples were essentially non-etherated. In Table 2 are listed d-spacings obtained from several samples.

Table 2,
d-Spacings For Aluminum Hydride Samples

<u>Sample No.113</u> <u>94% Hydride</u>	<u>Sample No.115</u> <u>> 96% Hydride</u>	<u>Sample A-16</u> <u>87% Hydride</u>
5.34	5.34	4.48
4.57	4.57	4.30
4.35	4.33	4.14
3.67	3.75	3.32
3.50	3.46	3.23
3.22	3.23	2.67
3.04	3.06	2.46
2.88	2.88	2.43
2.69	2.76	2.24
2.40	2.47	2.15
2.31	2.32	2.10
2.26	2.28	2.05
2.08	2.08	1.98
1.99	1.99	1.92
1.76	1.76	1.78
1.71	1.71	1.74
1.66	1.61	1.68
1.53	1.57	1.62
1.44	1.53	1.52
1.34	1.44	1.43
1.23		1.25
		1.15

C. Discussion

It is worthwhile to speculate on the mechanism of polymerization of aluminum hydride. Zeil (6) determined force constants for Al-H bonds and Al-O bonds in the co-ordination compounds of aluminum hydride with tetrahydrofuran. For the Al-H bond $k = 1.8 \times 10^5$ dynes/cm. and for the Al-O bond $k = 4.0 \times 10^5$ dynes/cm. The fact that the Al-O bond is about twice as strong as the Al-H bonds makes it clear why the aluminum hydride etherate decomposes, giving off hydrogen, while still retaining ether. It also indicates that the freshly prepared aluminum hydride is not co-ordinated to ether since running it into an inert solvent would not break up the co-ordination compound. It seems likely that the "polymerization" which is observed in aluminum hydride solutions is connected with,

or may actually be, the formation of the etherate. Of course, this does not indicate the nature of the dissolved species other than it is not co-ordinated to the ether.

The action of the inert solvent or precipitating agent merely seems to precipitate the aluminum hydride before it co-ordinates with the ether. Once the hydride had been precipitated it remained non-etherated if it was precipitated as a non-etherate. In one experiment, a sample of the non-solvated hydride was treated with ether. After several hours the ether was removed by heating to 50°C. in vacuum. Upon re-analysis there was found to be no essential change in the material from the time that the non-solvated material was first made. This shows that once the aluminum hydride is non-solvated it will not co-ordinate with ether.

Although pentane was used most frequently as the precipitating agent, other agents were found to be suitable. Hexane and benzene were tried successfully although benzene took longer to remove after precipitation due to its higher boiling point. Presumably other liquids, which would not react with or act as a solvent for aluminum hydride, would also be suitable.

References

- (1) Finholt, Bond, and Schlesinger, J. Am. Chem.Soc. 69, 1199 (1947)
- (2) Stecher and Wiberg, Ber. 75, 2003 (1942)
- (3) Wiberg, Angew.Chem. 65, 19 (1953)
- (4) Lonquet-Higrens, J.Chem.Soc. (1946), 139
- (5) Schumb, J.Am.Chem.Soc. 65, 1692 (1943)
- (6) Dr. Werner Zeil, Private Communication

